# MCM-41-supported ruthenium carbonyl cluster-derived catalysts for asymmetric hydrogenation reactions

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# ABSTRACT

Keywords: Ruthenium carbonyl cluster Functionalized MCM-41 Hydrogenation catalysts Asymmetric catalysis The anionic ruthenium carbonyl cluster  $[Ru_4(\mu-H)_3(CO)_{12}]^-$  has been ion-paired with (3-chloropropyl)trimethoxysilyl-cinchonidium or sparteinium groups chemically bound to the surfaces of MCM-41  $[(MCM-41-)(-O)_3SiCH_2CH_2CH_2NR_3^+Cl^-, NR_3 = cinchonidine or sparteine]$ . The resultant materials have been characterized before and after use as hydrogenation catalysts by IR, XPS, and TEM. The molecular identity of the cluster is retained in the fresh catalysts, but under hydrogen pressure ( $\geq$ 30 bar) the carbonyl groups are lost. Ruthenium (0) and a small amount of Ru<sup>2+</sup> can be observed on the fresh catalyst by XPS, while the used catalyst shows only Ru(0). TEM micrographs show retention of the MCM structure and no observable aggregation of metal. Under optimal conditions, good ( $\leq$ 75%) and observable ( $\leq$ 30%) enantioselectivities are obtained for the hydrogenations of methyl pyruvate and acetophenone, respectively. The enantioselectivity of the catalyst towards methylpyruvate hydrogenation is retained even with relatively high turnovers. This behavior is in sharp contrast to that of the Chini cluster [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup>, derived analogous catalyst reported earlier by us.

# 1. Introduction

Nanocatalyst

Insoluble polymer-supported homogeneous catalysts are of interest since they provide a simple and easy method for the separation of the catalyst [1–7]. In so far as asymmetric homogeneous catalysts are concerned, grafting of such catalysts onto a solid support is a viable strategy, but involves multi-step syntheses of expensive chiral ligands, and/or functionalization of a given support with such ligands [6,8–12]. Another strategy that has been the focus of much research avoids the costly synthesis of expensive ligands and/or organometallic complexes. Here a conventional heterogeneous catalyst such as platinum or Raney nickel is modified by treatment with easily available chiral substances [13–33]. Although the overall success by this approach has been limited, platinum on alumina modified by cinchona alkaloids has been found to be a particularly effective catalyst for the enantioselective hydrogenation of  $\alpha$ -ketoesters in general and

pyruvate esters in particular. After the name of its discoverer, this reaction is commonly referred to as the Orito reaction.

In our earlier work we showed that Orito-type catalysts could be made by ion pairing anionic platinum carbonyl clusters with (3chloropropyl)trimethoxysilyl-cinchonidium functionalized MCM-41 [34,35]. These catalysts were effective for the asymmetric hydrogenation of methyl pyruvate; significant enantioselectivities were also observed. Importantly, no enantioselectivity could be obtained with an analogous material where fumed silica was used as the support.

The work presented here was undertaken with the following objectives. First, to find out if any asymmetric catalysts for methyl pyruvate hydrogenation could be prepared by using a carbonyl cluster of some other metal such as ruthenium. Proving that the Orito reaction is not an exclusive attribute of platinum has important practical and mechanistic implications. It may lead to the development of asymmetric heterogeneous catalysts of other metals, and practical applications of such catalysts on a wider scale. Also, this would provide direct support for the recently suggested mechanism [13–16]. From the available experimental and theoretical evidence, an energetically favored interaction between the cinchona modifier and one specific prochiral face of the substrate seems to be the origin of enantioselectivity. An

obvious corollary of this mechanistic hypothesis is that a change of the metal may not have a major effect on the enantioselectivity as long as the metal of choice is effective for hydrogenation. However, a drastic drop or total disappearance in enantioselectivity is expected if either the chiral modifier or the prochiral substrate is changed. In view of this, the second objective of the work is to investigate the effect of changing chiral modifier from cichonidine to sparteine, another chiral tertiary amine, and methyl pyruvate to acetophenone, a substrate for which low enantioselectivity could be obtained with the cinchona-modified platinum catalyst [34,35].

Thus, this paper describes the synthesis, characterization and performance evaluation of  $[Ru_4(\mu-H)_3(CO)_{12}]^-$  cluster-derived catalysts, supported on cinchonidine- or sparteine-functionalized MCM-41. We find that, with both the catalysts, observable ee's are obtained in the hydrogenation of methyl pyruvate and acetophenone. The cinchonidium–methyl pyruvate combination is found to produce good enantioselectivity. In fact, for methyl pyruvate hydrogenation, the performance of the cinchonidium-based ruthenium catalyst is distinctly better than that of the platinum analogue. Good enantioselectivities accompanied by good turnovers are obtained and the drop in enantioselectivity with conversion is far less drastic.

# 2. Experimental

# 2.1. Chemicals

All preparations and manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (toluene over Na/benzophenone; methanol over Mg-turnings/iodine), distilled under nitrogen, and used immediately. Triruthenium dodeca-carbonyl, cetyltrimethylammoniumchloride, Ludox HS-30 colloidal silica solution, (3-chloropropyl)trimethoxysilane, cinchonidine, sparteine, methyl pyruvate, methyl lactate, acetophenone, 1-phenylethanol, bis(triphenylphosphoranylidine) ammonium chloride (PPN) were obtained from Aldrich, USA. Heptane, hexane, methanol and toluene were purchased from Merck India Pvt. Ltd. MCM-41 [36], [Ru<sub>4</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>12</sub>] [37–39] and [Ru<sub>4</sub>( $\mu$ -H)<sub>3</sub>(CO)<sub>12</sub>]<sup>-</sup> [40] were synthesized according to the literature procedures.

#### 2.2. Instruments

The freshly prepared catalysts were characterized by the solid state (KBr pellet) FTIR spectroscopic technique using a Thermo Nicolet 320 FTIR spectrophotometer. EDAX analysis was performed with an embedded energy-dispersive X-ray spectrometer available with qualitative and quantitative spectral analysis and X-ray mapping. The instrument used for the TEM study was a JEOL 2010F 200 kV, field-emission TEM. Generally, a high voltage (120–200 keV) finely focused electron beam is passed through a thin (50–200 nm) solid sample. Contrast is derived by electrons scattering from atoms in the material. Specific surface area and porosity were determined with a Micromeritics ASAP 2010 surface analyzer. BET were determined using 1–5 g of 100–200 mesh

#### Table 1

Elemental analysis data

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samples, with N<sub>2</sub> and He as the analysis and back fill gases. For XPS studies, a VG Microtech Multilab ESCA 3000 spectrometer was used. All the hydrogenation reactions were carried out in an autoclave. Conversions and enantioselectivities of the hydrogenation reactions with different substrates were monitored by a gas chromatographic technique with a FID detector (Shimadzu GC-2014 gas chromatograph) using a chiral capillary column (112-2562 CYCLODEXB, from J & W Scientific, length 60 m, inner diameter 0.25 mm, film 0.25  $\mu$ m). All hydrogenated products were initially identified by using authentic commercial samples of the expected products. For methyl pyruvate hydrogenation, the *R* isomer of methyl lactate was found to be the major product. For 1-phenylethanol, the absolute configuration was not determined but one enantiomer was observed to be the major component on the basis of GC experiments.

Functionalization of MCM-41 with (3-chloropropyl)trimethoxysilane and cinchonidine was carried out according to the literature methods [35,41]. Functionalization of chloropropylsilane group containing MCM-41 with sparteine was carried out in a similar fashion.

#### 2.3. Synthesis of catalysts 1a and 1b

Dried cinchonidine-modified functionalized support (MCM-41) (1 g) was added to a preformed orange methanolic solution (15 mL) of K[Ru<sub>4</sub>( $\mu$ -H)<sub>3</sub>(CO)<sub>12</sub>] (0.2 g) under carbon monoxide atmosphere. The mixture was stirred at 25 °C for 48 h. The solid material was filtered off, washed thoroughly with dry methanol, and then dried under CO atmosphere. Synthesis of catalyst **1b** was carried out in a similar fashion using sparteine-modified functionalized MCM-41 support.

#### 2.4. Catalytic experiments with 1a and 1b

The catalytic runs in general were carried out at 27 °C in 2 mL methanol contained in glass vials, with 50 mg catalysts [1(a/b)] (~3.7 × 10<sup>-3</sup> mM ruthenium). The glass vial was placed in an autoclave and a hydrogen pressure in the range of 20–70 bar was applied while stirring. At the end of the catalytic run, the reaction mixture was subjected to a GC chiral column and the extent of conversion was calculated on the basis of the ratio of the areas of the starting material and the product.

#### 3. Results and discussion

# 3.1. Synthesis and characterization of $[Ru_4(\mu\text{-}H)_3(\text{CO})_{12}]^-$ on the supports

The functionalizations of MCM-41 with trimethoxychloropropylsilane and chiral amines have been reported by others and by us [41,42]. We have also reported the complete characterizations of the surface sites after fucnctionalization with trimethoxychloropropylsilane and reaction with triethylamine by solid state NMR (<sup>29</sup>Si, <sup>13</sup>C, <sup>15</sup>N) [43].

Chemical analyses show that, for **1a** (cinchonidine) and **1b** (sparteine), the degree of functionalization with chloroproyl

Catalysts	Chloropropyl group <sup>a</sup> (mM/g)	Quaternary ammonium groups <sup>a</sup> (mM/g)	Ruthenium <sup>b</sup> (mM/g)	Surface Ru/Si ratio <sup>b</sup>
1a 1b	1.9 1.9	1.0 0.8	0.075 0.075	0.013 (fresh) 0.0053 (used) 0.011

<sup>a</sup> By elemental (C, H, N) analysis.

<sup>b</sup> Surface Ru/Si by XPS.





Fig. 1. FTIR spectrum of fresh catalyst 1a as KBr disc.

groups is similar:  $\sim 2 \text{ mM/g}$  (Table 1). However, differences in quaternary ammonium contents are observed. Degrees of incorporation of the quaternary ammonium groups seem to depend on the nature of the amines; more amine incorporation is observed with cinchonidine than with sparteine. A plausible explanation is that, due to different sizes and shapes, the two amines have different relative reactivities towards the chloropropyl groups. This is consistent with our earlier report where the steric bulk and shapes of the amine were found to have major effects on the degree of functionalization of MCM-41 [43].

The observed nitrogen and chloropropyl values indicate that, even after the treatment with excess amine, a large number of chloropropyl groups remain unreacted. Consistent with the bulk chloropropyl content derived from microanalysis, a significant amount of chlorine on the surface is also seen by EDAX. Chemical and EDAX analyses for all the samples did not show the presence of potassium, ruling out physical adsorption of K[Ru<sub>4</sub>( $\mu$ -H)<sub>3</sub>(CO)<sub>12</sub>]. For fresh and used catalysts **1a** and **1b**, the surface Ru/Si ratio has been calculated by XPS analysis. The observed data show that ruthenium incorporation is similar for both **1a** and **1b** (Table 1).

 Table 2

 Selected data on the hydrogenations of methyl pyruvate (Entries 1–18 for 1a; Entry 19 for 1b)

Entries	Amount of catalyst (mg)	Substrate (mM)	Pressure (bar)	Time (h)	TON (ee)
1	50	1	40	0.5	18 (45)
2	50	1	40	1.0	97 (48)
3	50	1	40	1.5	183 (55)
4	50	1	40	2.0	205 (62)
5	50	1	40	2.5	248 (70)
6	50	1	40	3.0	270 (75)
7	50	1	50	0.5	75 (45)
8	50	1	50	1.0	170 (55)
9	50	1	50	1.5	213 (59)
10	50	1	50	2.0	224 (65)
11	50	1	50	2.5	259 (65)
12	50	1	50	3.0	270 (60)
13	50	1	60	0.5	81 (42)
14	50	1	60	1.0	175 (62)
15	50	1	60	1.5	229 (62)
16	50	1	60	2.0	248 (69)
17	50	1	60	2.5	270 (59)
18	50	1	60	3.0	270 (53)
19	50	1	50	0.25	49 (35)

% Conversion and ee under varying reaction conditions. (*Reaction conditions*: methanol solvent (2 mL), temperature = 300 K. Each experiment was carried out in duplicate and the average values are given. Ruthenium content in 50 mg catalyst is 0.00375 mM.)

Freshly prepared **1a** and **1b** have IR bands (Fig. 1) that match well with those of  $[Ru_4(\mu-H)_3(CO)_{12}]^-$  [40] indicating incorporation of intact clusters (Scheme 1). The samples when stored under CO retain the IR bands for about an hour. This behavior is in contrast to that of supported platinum carbonyl clusters, where the CO ligands are lost very quickly [35,41]. The powder XRD patterns of the catalysts and the functionalized MCM-41 derivatives match well with the reported pattern of MCM-41 [44]. Surface areas  $(m^2/g)$  and pore size distributions as measured by BET for all the samples are very similar to those of their platinum analogues, which have been reported in our earlier publications [34,35]. In all the MCM-41 derivatives, 90% of the total pore volume comes from pores having radii within the range of 1–2 nm and  $\sim$ 1% of total pore volume is due to pores having radii within the range of 1.9–2.0 nm. Also for both the catalysts the internal surface area contributes more than 90% to the total surface area.



Scheme 1. Reaction sequence for functionalization and preparation of the catalysts.

# 3.2. Asymmetric hydrogenation of methyl pyruvate and acetophenone with **1a** and **1b**

In our earlier publications, the asymmetric hydrogenations of methyl pyruvate and acetophenone with functionalized MCM-41supported-platinum carbonyl clusters were reported [34,35]. The catalytic performances of **1a** and **1b** have also been tested with



**Fig. 2.** Plots of time versus % conversion ( $\blacksquare$ ) and ee ( $\blacktriangle$ ) for methyl pyruvate hydrogenation at (a) 40 bar (b) 50 bar and (c) 60 bar hydrogen pressure and at 300 K with catalyst **1a**.

these two prochiral substrates so that meaningful comparisons could be made between the performances of the platinum and the ruthenium catalysts. We first carried out control experiments to establish that, in solution, [PPN][Ru<sub>4</sub>( $\mu$ -H)<sub>3</sub>(CO)<sub>12</sub>] as a homogeneous catalyst has no observable catalytic activity for the hydrogenation of methyl pyruvate and acetophenone. Prolonged contact of a solution of [PPN][Ru<sub>4</sub>( $\mu$ -H)<sub>3</sub>(CO)<sub>12</sub>] with cinchonidine or sparteine led to the decomposition of the cluster. A large number of control experiments also proved that analogues of **1a** and **1b** with fumed silica as the support did not give any observable enantioselectivity in the hydrogenation of methyl pyruvate.

In contrast, both **1a** and **1b** catalyze the hydrogenation of methyl pyruvate with variable enantioselectivity that depends on the experimental conditions. This remarkable effect of the support is also noticed for the platinum cluster-based catalyst, and is probably because of restricted mobility of the metal particles within the narrow pores of MCM-41 [34,35]. Not surprisingly, **1a** is found to be distinctly more enantioselective than **1b**, and the maximum ee obtained under optimum conditions with **1a** and **1b** are ~75 and 35%, respectively. For this reason, the performance of **1a** has been evaluated under a wide set of conditions, selected data are presented in Table 2.

From the turnover data (TON) in Table 2, the following conclusions may be drawn. The TON increases as the pressure is raised from 40 to 50 to 60 bar (Entries 1, 7 and 13 in Table 2), but



**Fig. 3.** Plots of time versus % conversion ( $\blacksquare$ ) and ee ( $\blacktriangle$ ) for methyl pyruvate hydrogenation at (a) 50 bar and (b) 60 bar hydrogen pressure and at 300 K with catalyst **1b**.

the TON is less sensitive to pressure between 50 and 60 bar. More remarkable is the effect of pressure on ee. At 40 bar, the ee increases sharply with the increase in high TON (Entries 1-6), but at higher pressures (50 or 60 bar) a decrease in ee is observed at the higher TONs (e.g., Entries 12, 17, 18).

The ee initially increases with conversion, goes through a maximum, and then decreases with increasing conversions. This behavior, i.e. maximum ee at a certain conversion may be rationalized by a kinetic model similar to the one proposed by us in our earlier publication [35]. The rates of the enantioselective reaction as well as the deactivation of the enantioselective sites due to loss of chiral environment are both hydrogen pressuredependent, but the orders with respect to hydrogen pressure need not necessarily be the same. The quantitative validity of such a model and its statistical limitations, if any, will be addressed in our future work. As mentioned above, high ee values are accompanied by good TONs. These characteristics of **1a**, i.e. good ee with high TON and retention of moderate ee over a reasonably long period of reaction time (2-2.5 h), are in marked contrast to and a clear improvement over that of the platinum cluster-derived catalyst [34,35].

With the platinum catalyst, excellent enantioselectivity (>90%) could be obtained only for very low ( $\sim$ 10–15) turnovers over a short ( $\sim$ 15 min) reaction time. As the TON increases to 25 and 40, the ee drops to 30 and 10, and with  $\sim$ 100 turnovers the enantioselectivity is completely lost. In the classical Orito reaction,

![](_page_4_Figure_3.jpeg)

**Fig. 4.** Plots of time versus % conversion ( $\blacksquare$ ) and ee (▲) for acetophenone hydrogenation at (a) 50 bar and (b) 60 bar hydrogen pressure and at 300 K with catalyst **1a**.

maximum enantioselectivity and rate are achieved after a certain induction time [23,24], but no such induction time was observed with the platinum catalyst. With **1a** also high ee is not obtained at very low conversion, and the maximization of enantioselectivity at a specific conversion, as mentioned above, is probably a result of competing reactions with complex dependence on hydrogen pressure.

In view of the recently proposed mechanism, as discussed earlier, a substantial drop or complete disappearance of enantioselectivity is expected if the chiral modifier or the prochiral substrate is changed [13–16]. As described below, the relative performances of **1a** and **1b** as catalysts and methyl pyruvate and acetophenone as substrates do corroborate these expectations. **1b** is notably less enantioselective than **1a**: this is apparent from the time-monitored conversion and ee plots (Figs. 2 and 3). The best results using **1b** are obtained at 60 bar, when maximum ee ( $\sim$ 35%) is accompanied by a TON of  $\sim$ 49 (Entry 19 in Table 2). Unlike **1a**, with **1b** no maximum in ee is observed with time, and the enantioselectivity is rapidly ( $\sim$ 1.5 h) lost.

![](_page_4_Figure_7.jpeg)

**Fig. 5.** (a) XPS spectra of Si 2s, Cl 2p, Ru 3d and C 1s for catalyst **1a**. (b) Ru  $3p_{3/2}$  core level XPS spectra for fresh and used catalysts **1a** and fresh **1b**.

Table 3Hydrogenation of acetophenone with catalysts 1a and 1b under varying hydrogen<br/>pressures<sup>a</sup>

Entries	Catalysts	Pressure (bar)	Time (h)	TON (ee)
1	1a	40	8	89 (11)
2	1a	50	3	110 (27)
3	1a	60	1.5	89 (30)
4	1a	70	3	150 (9)
5	1b	40	6	68 (11)
6	1b	50	6	70 (10)
7	1b	60	6	81 (20)
8	1b	70	6	86 (12)

<sup>a</sup> Reaction conditions: methanol solvent (2 mL), 1 mM substrate, temperature = 300 K. Each experiment was carried out in duplicate and the average values are given. Ruthenium content in 50 mg catalyst is 0.00375 mM.

The hydrogenation of acetophenone is catalyzed by **1a** and **1b**, but with low enantioselectivity (Table 3). Both the catalysts under optimum conditions give low ( $\leq$ 30%) ee, but the performance of **1a** both in terms of activity (TON/time) and enantioselectivity is notably better than that of **1b**. Here again it may be noted that, unlike the platinum cluster-derived catalyst, where the best ee for acetophenone ( $\sim$ 49%) is associated with a TON of  $\sim$ 40, the ruthenium catalyst **1a** retains  $\geq$ 30% ee with reasonably high ( $\geq$ 89) TONs (Entry 3 in Table 3). The changes in the conversion and ee with respect to time could be measured for **1a**, and are found to be similar to that for methyl pyruvate (Fig. 4). Initially ee increases with conversion, reaches a maximum and then decreases, and this relationship between conversion and selectivity indicates that similar mechanisms probably operate for both the substrates.

# 3.3. XPS and TEM studies

XPS results from **1a** and **1b** are very similar, thus, since **1b** only gives modest enantioselectivity, the TEM studies have been confined to **1a**. As mentioned earlier (Section 3.1) the Ru/Si ratios of both **1a** and **1b** are very similar in the freshly prepared material, but in used **1a** this ratio drops to about half of that in the fresh catalyst (Table 1). This probably indicates that there is some

migration of the surface ruthenium during catalysis. Due to the comparatively inferior performance of **1b**, used **1b** was not studied.

The XPS (Ru 3d) spectra of fresh and used **1a** are shown in Fig. 5a. Ruthenium 3d core level overlaps with that of carbon 1s and deriving direct information is therefore difficult. However, oxidation state information could be obtained from other core levels and it is for this reason that the Ru  $3p_{3/2}$  core level has been analyzed. A careful analysis of the fresh catalysts (**1a** and **1b**) surface shows a broad Ru  $3p_{3/2}$  peak (Fig. 5b), and hints at the presence of small amounts of oxidized ruthenium along with some zero valent ruthenium of the cluster anion. A deconvolution analysis of Ru  $3p_{3/2}$ , indeed, shows that, though the majority of the ruthenium is present in the zero oxidation state, there is a small amount of high valent ruthenium, most probably Ru<sup>2+</sup> (Fig. 5b) [45,46].

In our earlier publication that described platinum clusterderived catalytic systems, similar observations were made. Along with zero valent platinum of the cluster anion, small amounts of a Pt<sup>2+</sup> species, most probably PtCl<sub>2</sub> with co-ordinated organic moieties, were observed. The latter was thought to arise from the reaction between the clusters and excess tetralkylammoniumchloride functionalities of the support. It may be noted that a survey-scan of fresh 1a (Fig. 5a) clearly indicates the presence of chloride ions. The presence of Ru<sup>2+</sup> on the surfaces of freshly prepared 1a may thus be rationalized by invoking a similar reaction between the ruthenium cluster and the chloride anions. Such reactions are known to be especially facile for ruthenium carbonyl clusters, and therefore it is unlikely that the high-valent ruthenium arises from any other ruthenium species. The XPS spectrum of used **1a** exhibits exclusively zero-valent ruthenium around 462.5 eV. Presumably under the catalytic reaction conditions involving high hydrogen pressures, the Ru<sup>2+</sup> species is reduced to zero-valent ruthenium. It may be noted that it is the ruthenium of the cluster anion (zero oxidation state ruthenium) and not the Ru<sup>2+</sup> species that is expected to take part in the ion pair formation with the surface cinchonidium functionalities. In other words, it is the zero oxidation state ruthenium of the cluster that is expected to be the catalytically active species.

![](_page_5_Figure_10.jpeg)

Fig. 6. TEM images of 1a (a) fresh and (b) used.

TEM images recorded on fresh catalyst clearly show the hexagonal array of MCM-41 and no distinct Ru-particles are observed at the resolution of TEM used by us (Fig. 6). In fact, well dispersed Ru-nanoclusters (Ru<sub>4</sub>) in the pores of MCM-41 should be smaller than 1 nm, i.e., smaller than the fringe width of MCM-41, and hence not likely to be observed. On the used catalysts also, MCM-41 fringes are clearly observed, indicating that the MCM-41 support structure is intact even after the reaction. On the used catalyst there is no evidence of Ru-aggregation leading to larger particles.

It may be noted that, in the platinum cluster-derived catalyst, extensive aggregation leading to the formation of larger metal particles have been observed, and is thought to be the main reason behind the rapid loss in enantioselectivity [34,35]. The ability of **1a** to retain enantioselectivity over considerably higher TON may partly be due to the fact that extensive aggregation of ruthenium particles does not take place during the course of the hydrogenation. The main reason for the deactivation of the enantioselective sites in this case is probably the migration of the surface ruthenium away from the chiral environment to the bulk. As mentioned earlier, the Ru/Si ratio in the used catalyst as measured by XPS is about half of that in the fresh catalyst, which does suggest such migration.

The recyclibality of **1a** both in terms of activity and selectivity has been evaluated by carrying out two successive batches under the conditions of Table 2 (Entries 6 and 11). While the conversions (TON) are comparable within experimental errors, there is a significant (>10%) drop in enantioselectivity. A kinetic model that accounts for these and other related observations will be the subject matter of our future publications.

#### 4. Conclusion

The ruthenium carbonyl cluster,  $[Ru_4(\mu-H)_3(CO)_{12}]^-$ , supported on cinchonidinium-functionalized MCM-41 is an effective precursor for an enantioselective catalyst for the hydrogenation of methyl pyruvate. Good enantioselectivity could be obtained even with high turnovers, which is not possible with the analogous platinum cluster-derived catalysts [34,35]. A change of cinchonidine to sparteine as the chiral modifier, or of methyl pyruvate to acetophenone as the prochiral substrate, results in significant loss of enantioselectivity, which is consistent with the current mechanistic hypothesis for the platinum-alumina catalyst-based Orito reaction [13-16]. A kinetic model that involves a hydrogen pressuredependent deactivation of the enantioselective sites fits well with the experimental data, and is consistent with XPS and TEM data.

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